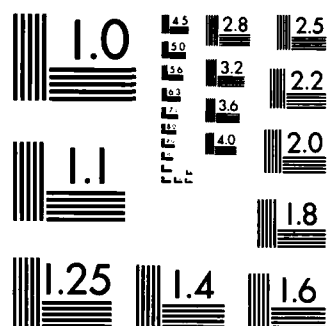END

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"A Two-Terminal Microelectrochemical Diode with Contact Spacing of

About One Micron: A Device Based on One Solution Redox Couple and

One Electrode-Confined Redox Couple"

by

Gregg P. Kittlesen and Mark S. Wrighton

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ABSTRACT

A microelectrochemical diode can be fabricated by functionalizing one of two identical, adjacent platinized Au microelectrodes of an eight electrode microelectrode array with a redox polymer, $[(BPQ^{2+/+})_n]$, derived from an N,N'-dibenzyl-4,4'-bipyridinium monomer. The microelectrode array consists of eight Au microelectrodes each about 50 microns long, 2.3 microns wide, and 0.1 microns thick and separated from each other by about 1.3 micron. The array is fabricated on a Si_3N_4 surface chemically deposited on a Si/SiO_2 substrate using conventional microfabrication procedures. Diode behavior is found in aqueous electrolyte solution containing the $Ru(NH_3)_6^{3+/2+}$ redox couple which responds reversibly at a platinized Au electrode. Rectifying behavior is obtained, because a micro electrode modified with greater than $\sim 10^{-9}$ mol/cm^2 of the $[(BPQ^{2+/+})_n]$ polymer is capable of reducing the oxidized form of the redox couple $(Ru(NH_3)_6^{3+})$ but is incapable of oxidizing the reduced form of the redox couple $(Ru(NH_3)_6^{2+})$. Reduction of the oxidized form of the redox couple can only be effected at a fast rate when the polymer has a significant fraction of the monomer units in the BPQ^+, one-electron reduced, state. When the negative lead of a power supply is attached to a $[(BPQ^{2+/+})_n]$-derivatized microelectrode and the positive lead is attached to an adjacent, naked microelectrode current flows when the applied potential approaches the difference in the formal redox potentials of the $Ru(NH_3)_6^{3+/2+}$ and $[(BPQ^{2+/+})_n]$ redox couples, about 0.4 V. When the potential is applied in the opposite sense, no current flows.

The results demonstrate that molecule-based diodes can be fabricated and properties such as threshold voltage can be rationally altered by variation in the molecular materials used.

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A TWO-TERMINAL MICROELECTROCHEMICAL DIODE WITH CONTACT

SPACING OF ABOUT ONE MICRON: A DEVICE BASED ON ONE SOLUTION

REDOX COUPLE AND ONE ELECTRODE-CONFINED REDOX COUPLE

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ABSTRACT

A microelectrochemical diode can be fabricated by functionalizing one of two identical, adjacent platinized Au microelectrodes of an eight electrode microelectrode array with a redox polymer, $[(BPQ^{2+/+})_n]$, derived from an N,N'-dibenzyl-4,4'-bipyridinium monomer. The microelectrode array consists of eight Au microelectrodes each about 50 microns long, 2.3 microns wide, and 0.1 microns thick and separated from each other by about 1.3 micron. The array is fabricated on a Si_3N_4 surface chemically deposited on a Si/SiO_2 substrate using conventional microfabrication procedures. Diode behavior is found in aqueous electrolyte solution containing the $Ru(NH_3)_6^{3+/2+}$ redox couple which responds reversibly at a platinized Au electrode. Rectifying behavior is obtained, because a micro electrode modified with greater than $\sim 10^{-9}$ mol/cm^2 of the $[(BPQ^{2+/+})_n]$ polymer is capable of reducing the oxidized form of the redox couple $(Ru(NH_3)_6^{3+})$ but is incapable of oxidizing the reduced form of the redox couple $(Ru(NH_3)_6^{2+})$. Reduction of the oxidized form of the redox couple can only be effected at a fast rate when the polymer has a significant fraction of the monomer units in the BPQ^+, one-electron reduced, state. When the negative lead of a power supply is attached to a $[(BPQ^{2+/+})_n]$-derivatized microelectrode and the positive lead is attached to an adjacent, naked microelectrode current flows when the applied potential approaches the difference in the formal redox potentials of the $Ru(NH_3)_6^{3+/2+}$ and $[(BPQ^{2+/+})_n]$ redox couples, about 0.4 V. When the potential is applied in the opposite sense, no current flows.

The results demonstrate that molecule-based diodes can be fabricated and properties such as threshold voltage can be rationally altered by variation in the molecular materials used.

We wish to report the fabrication and characterization of a
microelectrochemical diode based on molecular materials as the
crucial elements where one redox material is confined to one of
two Au electrodes and another redox material is in solution,
Scheme I. The electrode-confined redox polymer, $[(BPQ^{2+/+})_n]$,

$$A^{3+/2+} = Ru(NH_3)_6^{3+/2+}$$
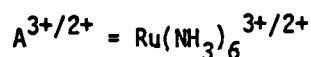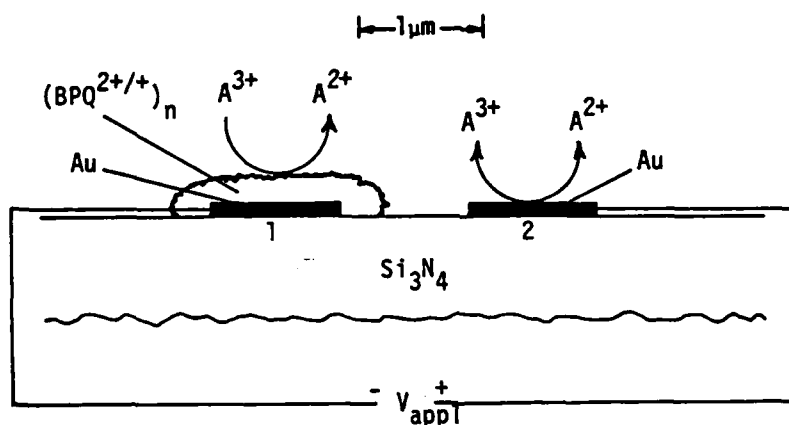
Scheme I. Representation of the microelectrochemical diode
described in this article.

is derived from the monomer $\underline{I}$ by hydrolysis of the -Si-OMe groups


$$\underline{I}$$
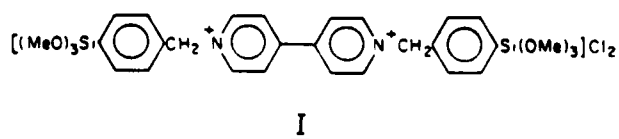
to form a polysiloxane.[1] Recent reports from this laboratory
describe several new kinds of microelectrochemical devices where
molecular materials are "active" elements in achieving the device
function.[2-6] The general aim of the research is to develop
approaches to the specific functionalization of microelectrode

arrays with molecule-based reagents to achieve particular overall functions such as transistor- and diode-like behavior when the arrays are immersed in electrolyte solutions. The devices do not involve the use of single molecules. Rather, assemblies of molecules and particular arrangements of these assemblies with arrays of microelectrodes are exploited to achieve functions that mimic the functions of solid state devices. The device dimensions, e.g. contact-contact spacing, are not what would be regarded as characteristic of small molecules, but fall in a regime that is established by state-of-the-art microfabrication techniques. Microelectrochemical diodes having contact-contact spacings of about 0.3 micron have recently been demonstrated.[5] It should be emphasized that this article concerns work related to combining known scientific principles to achieve a particular end result. The work represents a new kind of synthesis: preparation of aggregate structures which have an overall function.

At this point there is no expectation that microelectrochemical devices will displace solid state devices in their present uses. Rather, the microelectrochemical devices will likely be important in cases where the molecular properties are important. A major area of potential application is that of sensors of choooand biological substances where molecule-based materials may be essential in interfacing the chemical systems with biological systems. Additionally, the microelectrochemical devices provide new ways to characterize the charge transport properties of molecular materials,[4] and derivatization of

microelectrodes with molecular reagents allows testing of the understanding of derivatization processes. Finally, the small size and close spacing of microelectrodes in microelectrode arrays opens new kinds of electroanalytical experimentation associated with the diffusion properties of redox active substances in solution.[7,8]

The basis of the diode function for the device illustrated in Scheme I is that the solution redox couple, $Ru(NH_3)_6^{3+/2+}$, responds reversibly at naked (non-derivatized) platinized Au microelectrodes, but the $[(BPQ^{2+/+})_n]$-derivatized microelectrodes are incapable of oxidizing the $Ru(NH_3)_6^{2+}$ at any potential and only capable of reducing the $Ru(NH_3)_6^{3+}$ when the electrode potential is sufficiently negative to produce a significant concentration of the one-electron reduced polymer centers, BPQ^+. The point is that the $Ru(NH_3)_6^{3+/2+}$ species in solution will not penetrate the positively charged polymer and only interacts with the outermost portion of the $[(BPQ^{2+/+})_n]$ polymer that coats the electrode.[9] The formal potential of the $[(BPQ^{2+/+})_n]$ polymer is ~-0.55 V vs. SCE,[1] about 0.4 V more negative than the formal potential of the $Ru(NH_3)_6^{3+/2+}$ redox couple.[9] The redox reaction represented by equation (1) is thus 0.4 V downhill and the

$$[(BPQ^+)_n] + nRu(NH_3)_6^{3+} \longrightarrow [(BPQ^{2+})_n] + Ru(NH_3)_6^{2+} \quad (1)$$
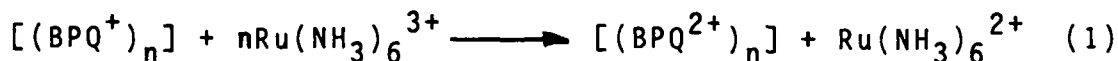
reverse is 0.4 V uphill. Thus, when the two redox reagents are arranged as in the device represented by Scheme I the current should only flow in a two terminal device when the power supply

has the negative lead attached to the $[(BPQ^{2+/+})_n]$-derivatized electrode and the applied potential is >0.4 V. When the potential is applied in the opposite sense the redox polymer would be in the $[(BPQ^{2+})_n]$ state and would be incapable of oxidizing any solution species thereby blocking the flow of current. Thus, the derivatizing reagent plays the two-fold purpose of controlling the threshold potential, by virtue of its formal potential, and of preventing the solution redox reagent from penetrating to the Au substrate, by virtue of its net positive charge and uniformity of coverage. If the difference in formal potentials of the two redox components is too small, or if the solution redox reagent can penetrate the electrode-confined redox reagent the diode will be "leaky". It should be pointed out here that our use of the term "diode behavior" is equivalent to "uni-polar current flow".

In principle, a combination of any two redox reagents that differ in their formal potential can be useful in a microelectrochemical diode as in Scheme I. The particular properties of the devices will depend on the charge transport properties of both the electrode-confined and the solution redox couples. The frequency of operation of microelectrochemical diode and transistor devices is expected to be much lower than for solid state devices since faradaic processes, involving movement of ions, are required in the switching.[2-6] Maximizing the frequency of operation involves considering device design and the molecular materials. Since the effective diffusion coefficient for charge transport through surface-confined redox

polymers is modest, 10^{-8} cm^2/s and lower, compared to the diffusion coefficient for the movement of a solution redox reagent, 10^{-5}-10^{-6} cm^2/s,[10] it is logical to aim for a polymer thickness that is as thin as possible while maintaining a coating sufficient to completely block the solution redox couple from the surface. In any case, the smallest contact-contact spacing possible will maximize the frequency. We now describe the fabrication and characterization of the diode represented by Scheme I.

EXPERIMENTAL

Microelectrode Arrays. Arrays of eight Au microelectrodes each 50 micron long, 2.3 micron wide, and 0.1 micron thick and spaced 1.3 micron apart were used in the work described in this article. Fabrication of the microelectrode arrays on p-Si/SiO$_2$/Si$_3$N$_4$ substrates has been described previously.[2-5] Prior to use each of the Au microelectrodes was modified by the electrochemical deposition of Pt onto the surface. The Pt was deposited from aqueous 0.1 $\underline{M}$ K$_2$HPO$_4$ containing 2 m$\underline{M}$ K$_2$PtCl$_4$. The charge passed in the deposition of Pt corresponds to the deposition of 8.6 x 10^{-7} mol/cm^2 of Pt. Such a treatment roughens the electrodes and closes the average spacing between the electrodes to approximately 1.0 micron, as established by microscopy.[5] The Pt deposition improves the electrochemical response to the solution redox couple Ru(NH$_3$)$_6$$^{3+/2+}$.

Chemicals. The solvent in all experiments was triply distilled H$_2$O. The supporting electrolyte used was commercially available KCl which was used as received. The solution redox reagent was obtained as the Cl$^-$ salt of the oxidized material, Ru(NH$_3$)$_6$Cl$_3$, from Strem Chemicals. This species was either used as received or partially reduced in aqueous KCl solutions by controlled potential electrolysis to give the desired ratio of Ru(NH$_3$)$_6$$^{3+}$ and Ru(NH$_3$)$_6$$^{2+}$. The surface derivatizing reagent $\underline{I}$ has been reported previously and was available from earlier studies.[1]

Electrochemical Equipment. Electrochemical plating of Pt onto the Au microelectrodes was accomplished using a Princeton Applied Research Model 173 potentiostat, a Model 175 voltage programmer,

and a Model 179 digital coulometer. Derivatization with reagent

$\underline{I}$ and the quantitative characterization of the devices was

carried out using a Pine Model RDE4 bipotentiostat. The two

terminal measurements were pe formed by connecting the working

electrode lead of the potentiostat to one microelectrode and the

counter and reference electrode leads to the other microelectrode

of the two-terminal device. In such a configuration the

potentiostat acts as a current follower. The current-potential

curves were recorded on a Kipp α Zonen BD91 XYY't recorder.

Potential step data were recorded on either the Kipp α Zonen

recorder or on a storage oscilloscope. When a reference

electrode was used, the reference electrode was a saturated

calomel electrode (SCE). All electrochemical measurements were

carried out in quiet solutions under Ar at 298 K.

Derivatization With Reagent $\underline{I}$. Selective derivatization of a

particular electrode of an array with $[(BPQ^{2+/+})_n]$ could be

achieved by electrochemically assisting the deposition of the

polymer. While holding electrodes not to be derivatized at 0.0 V

vs. SCE, the electrode to be derivatized is cycled between 0.0

and -0.75 V vs. SCE at 50 mV/s in an aqueous solution of 0.5 m$\underline{M}$ $\underline{I}$

and 0.2 $\underline{M}$ KCl/0.1 $\underline{M}$ K_2HPO_4. The cycling is continued until the

desired coverage of $[(BPQ^{2+/+})_n]$ is detected on the electrode.

The coverage is given by the integral of the cyclic voltammetric

wave, centered at -0.55 V vs. SCE, corresponding to the

interconversion of surface bound BPQ^{2+} and BPQ^+. Typically, the

coverage of BPQ^{2+} centers was about 10^{-8} mol/cm^2.

<u>Microscopy</u>. The microelectrode arrays were examined by electron microscopy using a Cambridge Mark 2A Stereoscan instrument with a resolution of 20 nm. Prior to examination, the arrays were coated with ~20 nm of Au to minimize problems from surface charging. Optical microscopy of completed electrode arrays prior to use was routinely carried out to ensure that the arrays were free of substantial defects. The optical microscopy was done up to a magnification of 1000X using a Bausch α Lomb MicroZoom microscope equipped with a Polaroid camera.

RESULTS AND DISCUSSION

<u>Derivatization of Au Microelectrodes with I</u>. Naked Au electrodes
show no electrochemical response in aqueous 0.1 $\underline{M}$ KCl solution,
except for the reduction and oxidation at the decomposition
potentials of the medium. The useful potential window for the Au
microelectrodes is about -0.8 to +0.6 V vs. SCE. Derivatization
of the microelectrodes using reagent $\underline{I}$ can be carried out as
described in the <u>Experimental</u>. The important results are that
(1) the coverage of $[(BPQ^{2+}\cdot2Cl^-)_n]$ can be controlled and in
particular (2) the redox polymer can be deposited specifically on
some electrodes and not others. For the purpose of preparing a
microelectrochemical diode it is noteworthy that a microelectrode
can be derivatized with $[(BPQ^{2+}\cdot2Cl^-)_n]$ while adjacent
microelectrodes are completely free of the redox polymer. The
coverage of the $[(BPQ^{2+}\cdot2Cl^-)_n]$ can be controlled because the
derivatization procedure is one which is based on an
electrochemical method[1] where coverage can be monitored during
the derivatization procedure. The coverage of the polymer can be
determined rather accurately by integrating the cyclic
voltammogram associated with the interconversion of the
$[(BPQ^{2+})_n]$ and $[(BPQ^+)_n]$ forms of the polymer. This method for
deptermining coverage is useful at sweep rates where the peak
current is directly proportional to sweep rate, typically less
than 200mV/s. Figure 1 shows a cyclic voltammogram for a
representative microelectrode that has been derivatized with $\underline{I}$;
the coverage in this instance is 3.4 x 10^{-8} mol/cm^2. The
thickness of such a polymer coverage is expected to be 0.15

microns, based on work on macroscopic electrodes.[9] Thus, the thickness of the redox polymer is substantially less than the contact-contact spacing of the microelectrode array. Experimentally, we find that the $[(BPQ^{2+})_n]$ does not "connect" adjacent microelectrodes at the coverages used in this work. Both optical and electron microscopy confirm that the polymer can be confined to one microelectrode situated between two that are naked. The electrochemical response of the microelectrode-confined polymer in 0.1 $\underline{M}$ KCl is essentially that expected based on studies of the same polymer on macroscopic electrodes.

Comparison of the Electrochemical Response of $Ru(NH_3)_6^{3+/2+}$ at Naked and Derivatized Electrodes.

Figure 2 shows the comparison of the electrochemical response of $Ru(NH_3)_6^{3+}$ and a 1/1 ratio of $Ru(NH_3)_6^{3+/2+}$ at a naked microelectrode compared to a derivatized microelectrode. The derivatized microelectrode is that characterized by the cyclic voltammogram shown in Figure 1. The particular arrangement of microelectrodes used is illustrated in Scheme II. As the data in Figure 2 illustrate, the
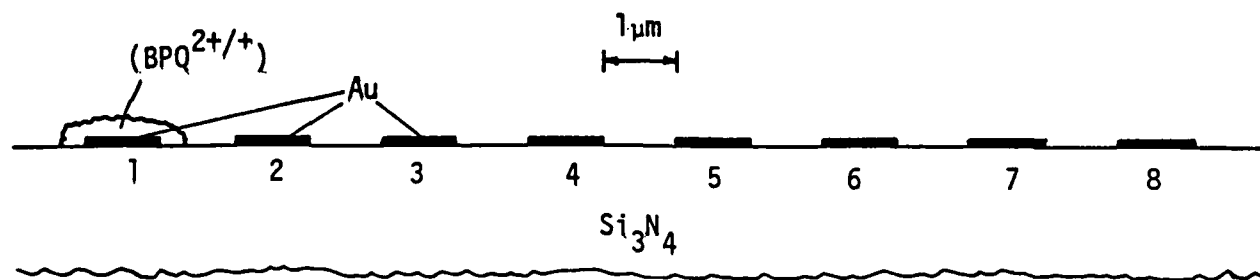
Scheme II. Representation of the microelectrode array characterized by the data in Figures 1-4.

electrochemical response of the $Ru(NH_3)_6^{3+/2+}$ at the naked electrodes is what would be expected for a reversible redox couple. When only the $Ru(NH_3)_6^{3+}$ is present in the bulk solution the electrochemical reduction onsets near the formal potential of about -0.2 V vs. SCE. However, at the $[(BPQ^{2+/+})_n]$-derivatized microelectrode the onset of electrochemical reduction is substantially more negative; the onset is close to the onset of the electrochemical reduction of the $[(BPQ^{2+})_n]$ state of the polymer. The lack of an onset of reduction of $Ru(NH_3)_6^{3+}$ close to the formal potential of the solution redox couple is consistent with the conclusion that the $[(BPQ^{2+})_n]$ polymer prevents the oxidized species from penetrating to the surface of the electrode. Similar findings have been reported for macroscopic electrodes derivatized with I or a related N,N'-dialkyl-4,4'-bipyridinium based reagent.[9]

The data in Figure 2 illustrate that the reduction of $Ru(NH_3)_6^{3+}$ is blocked at the $[(BPQ^{2+})_n]$-coated electrode. We have interpreted the result as being due to the fact that the polycationic polymer precludes penetration of the positively charged Ru complexes. The data can be accommodated by concluding that there is only slow penetration of the Ru species and/or slow electron exchange between $Ru(NH_3)_6^{3+/2+}$ within the film and the electrode. Whatever the interpretation the $[(BPQ^{2+})_n]$-coated electrode allows the fabrication of a diode, since only the reduction process occurs at the derivatized surface.

Note that at the sweep rates used in the experiments summarized by Figure 2 the current-potential scans are not what

would be observed at a macroscopic electrode. At macroscopic electrodes a cyclic voltammetry wave[11] would be observed with a well-defined current peak on the forward and reverse sweep. The width of the microelectrodes is sufficiently small that the consequences of diffusion processes are different at the sweep rates shown and give rise to what appear to be steady state current-potential curves at a macroscopic electrode.[7,8,12] At the coverage of polymer and $Ru(NH_3)_6^{3+}$ used, the steady state current for the reduction of $Ru(NH_3)_6^{3+}$ on the plateau portion of the current-potential curve is the same for the naked and the derivatized electrodes. The current density for reduction is of the order of 4 mA/cm^2, a value consistent with the known charge transport properties of the $[(BPQ^{2+/+})_n]$ polymer.[9] However, an order of magnitude increase in the concentration of the $Ru(NH_3)_6^{3+}$ would yield a steady state current for the derivatized electrode that is limited by the charge transport properties of the redox polymer. For the conditions shown the steady state currents in the plateau region of the curves depend only on the concentration of the solution species and its diffusion properties.

An especially significant finding with respect to being able to demonstrate a two-terminal diode is that the derivatized electrode is incapable of oxidizing the reduced form of the solution redox couple, no matter what electrode potential is used, Figure 2. The data for a solution that is 1 m$\underline{M}$ in both halves of the redox couple shows that neither the 3+ nor the 2+ is capable of penetrating the $[(BPQ^{2+})_n]$ polymer. The point is

that the BPQ^{2+} units at the outermost portion of the polymer are incapable, thermodynamically, of oxidizing the $Ru(NH_3)_6^{2+}$ species and the polycationic material uniformly coats the electrode surface precluding the penetration of the positively charged solution species to the electrode. The data in Figure 2 for the 1/1 ratio of the $Ru(NH_3)_6^{3+/2+}$ species establishes that the naked electrodes can be used to oxidize the reduced species or reduce the oxidized species. Under the same conditions the derivatized electrode is only capable of reducing the oxidized species. These results establish that a two-terminal diode of the type represented in Scheme I is possible.

Two-Terminal Microelectrochemical Devices. Figure 3 shows the electrochemical behavior of two-terminal microelectrochemical devices employing a microelectrode array like that represented in Scheme II. The array is that characterized by the data in Figures 1 and 2. When two of the naked electrodes are used the current-voltage curves are as would be expected for two identical, reversible electrodes. Application of a potential difference, in either direction between any two naked microelectrodes of the array yields current flow just beyond an applied potential of zero volts. The current-voltage curves are symmetrical about zero volts and the plateau of current is controlled by the concentration of the $Ru(NH_3)_6^{3+/2+}$ redox couple and the diffusion properties.

One interesting feature of the two-terminal device based on the two naked electrodes is that the plateau current exceeds the plateau current when one naked electrode is examined as shown in

Figure 2. The approximately 4 nA current at a single electrode in the plateau regime is to be contrasted with the approximately 8 nA found in the two-terminal experiment, Figure 3. The significant difference found in the two experiments is that the microelectrodes of the array are sufficiently close to each other that when one electrode regenerates the species consumed at the other there is a positive feedback that increases the availability of redox active material. This phenomenon is to be elaborated elsewhere.[13]

The important result relating to two-terminal devices is given by the current-voltage curve between a naked and a derivatized electrode, Figure 3. As illustrated, current only flows when the negative lead of the power supply is connected to the $[(BPQ^{2+/+})_n]$-derivatized electrode. When the potential is applied in the opposite sense, positive lead to the derivatized electrode, no current passes, because the $[(BPQ^{2+/+})_n]$-coated electrode is incapable of oxidizing the reduced form of the $Ru(NH_3)_6^{3+/2+}$ redox couple. The plateau current from the diode in "forward bias" is the same as the plateau current for the two-terminal device based on two naked electrodes. This result shows that the magnitude of the positive feedback is the same at the $[(BPQ^{2+/+})_n]$-derivatized electrode as at a naked electrode. Since the magnitude of the feedback is dependent on electrode geometry, the fact that the derivatized electrode can give the same magnitude effect as a naked electrode indicates that there is little geometrical consequence associated with the deposition of a small amount of polymer on the electrode surface. Further,

the fact that the steady-state current is the same for the two-terminal diode and the device based on two naked electrodes means that the coverage of polymer is sufficiently low that the charge transport properties of the polymer do not inhibit the steady-state current, even when there is positive feedback from the adjacent naked electrode to increase the current density compared to that shown in Figure 2. The threshold voltage for the two-terminal diode is consistent with the data given in Figure 2. The difference in the onset of current in the 1/1 $Ru(NH_3)_6^{3+/2+}$ solution at the naked and derivatized electrodes is $_\mu 0.2$ V, Figure 2, and in the two-terminal device, Figure 3, the onset of current under forward bias occurs at $_\mu 0.2$ V. From the data in Figure 3 it is clear that a microelectrochemical diode can be fabricated, regarding a diode as a two-terminal device where current will only flow upon application of potential in one of the two directions.

The difference in the formal potentials of the $[(BPQ^{2+/+})_n]$ and $Ru(NH_3)_6^{3+/2+}$ redox couples is likely about as small as would be desirable, because a small difference would give rise to some "leakage" currents. Assuming that the polymer is not a limitation in terms of charge transport properties, it is possible to have substantial leakage current in reverse bias when the self-exchange rates of the redox partners is large.[14-16] Fundamental studies of the reactions of the outermost layer of the redox polmyer with "outer-sphere" solution redox reagents can yield data necessary to make predictions concerning the characteristics of diodes like that reported here.

A major difference between a solid state diode and the diode demonstrated by the data in Figure 3 is that the solid state diode involves the use of materials that are good electronic conductors while the microelectrochemical diode operates because two dissimilar redox reagents are interfaced. The redox reagents employed are not good conductors and the practical consequence is that the frequency of operation of the electrochemical diode is limited by the modest charge transport properties of redox systems of the sort employed here. One purpose in demonstrating the diode represented by Scheme I is that the use of only one immobilized redox couple, the $[(BPQ^{2+/+})_n]$, and one in solution allows the device to operate at a higher frequency than if both redox couples are immobilized as in the device recently demonstrated and represented by Scheme III.[5] The device
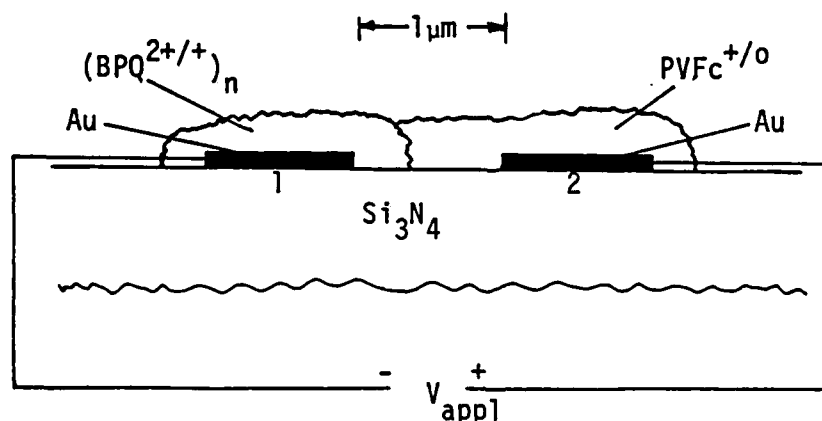
Scheme III. A two-terminal microelectrochemical diode based on two immobilized redox polymers that are in contact with each other.[5]

represented by Scheme III involves the use of two materials with poor charge transport properties in that the effective diffusion

coefficient for charge transport of the polyvinylferrocene system, $PVFc^{+/0}$,[17] and the $[(BPQ^{2+/+})_n]$[9] is small. For each of these two materials the effective diffusion coefficient for charge transport is less than 10^{-8} cm^2/s.[9,17] This means that the switching time for the device is of the order of seconds when the distance between the two electrodes is about one micron. When only one redox couple is immobilized, as in the device described here, the solution species can have a diffusion coefficient which is much larger, and the device frequency can be improved because the immobilized system can be relatively thin. The disadvantage, of course, is that there must be a solution redox reagent present in the solution, whereas the device represented by Scheme III will operate without any other redox active material in the ambient.[5]

Figure 4 illustrates some data demonstrating that the diode characterized by the steady-state data in Figure 3 can be cycled on and off relatively rapidly, compared to the on and off rate of the device represented by Scheme III.[5] Compared to a solid state device the diode characterized by the data in Figures 3 and 4 is still slow, however.[18] The data in Figure 4 show that a complete cycle from off to on and back to off can be completed in less than 10 s. The time to switch from off to on is longer than the time to switch from on to off. The spike of current following a change in potential is associated with the charge and discharge of the double layer of the metallic electrodes in contact with the electrolyte solution and with the oxidation and reduction of the surface bound polymer. The response time of the

X-Y recorder is too slow to follow the current spike, but an oscilloscope recording shows that the polymer can be completely reduced from the 2+ to the + state or completely oxidized from the + to the 2+ state in less than 0.2 s in 0.1 $\underline{M}$ KCl, but without $Ru(NH_3)_6^{3+/2+}$ present in the medium. This switching speed for the polymer is in accord with previous measurements.[1]

The curious feature of the data shown in Figure 4 is that the current goes up, then down, and up again to a steady state value in stepping the potential from an off to on value. This curious behavior is not found at higher concentrations of the $Ru(NH_3)_6^{3+/2+}$ redox couple. Moreover, the behavior for two naked electrodes is simpler: the current reaches the steady-state value within 0.1 s upon application of potential steps from -0.6 to +0.6 to -0.6 volts applied. It would appear that the unusual current-time data upon turning on the diode by a potential step from -0.6 to +0.6 volts applied, Figure 4, is due to loss of potential control at the early times. This phenomenon is sometimes observed for polymer modified electrodes and results in similar problems.[19] In this case the effect is somewhat more subtle, because in a two-terminal electrochemcial device the electrodes are not under potential control relative to a reference. The actual potential of the two electrodes, relative to a reference, depends on the concentrations of the two halves of the redox couple, the diffusion properties of the two halves of the redox couple, and the kinetics for the two halves of the redox couple. Scheme IV illustrates the potentials, at steady-

state, of the electrodes in the two-terminal devices represented by the steady-state data given in Figure 3. Upon switching the potential from the off to the on state of the diode the early times are involved with the reduction of the polymer from the 2+ to the + state and no reduction of the $Ru(NH_3)_6^{3+}$ occurs at the $[(BPQ^{2+})_n]$-coated electrode until reduced centers appear at the outermost portion of the polymer. However, while the reduction of the polymer is occurring oxidation of $Ru(NH_3)_6^{2+}$ is occurring
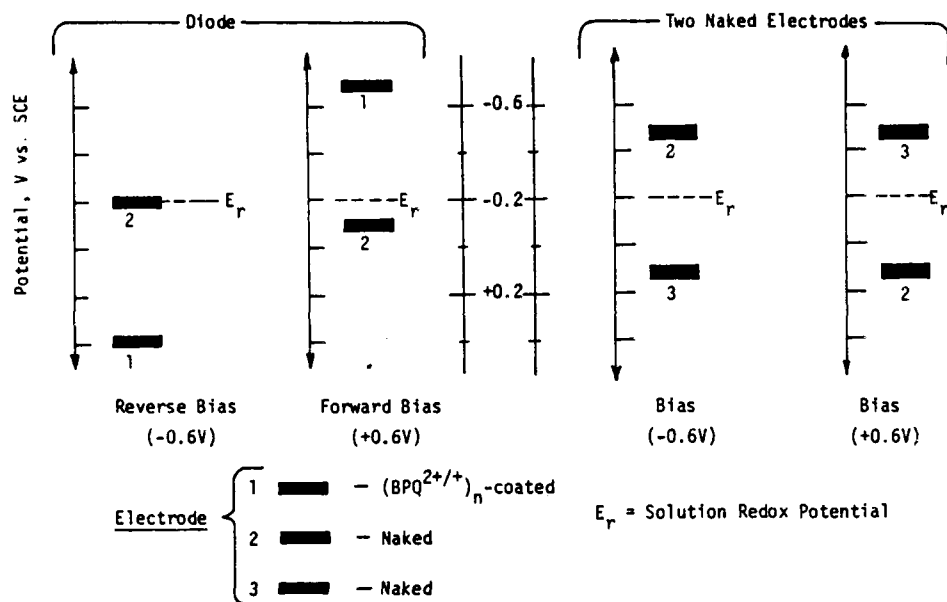
Scheme IV. Actual potentials of the two electrodes (at steady-state) of the two-terminal devices characterized by the data in Figure 3. These values are estimates from the assumption that the kinetics for oxidation of $Ru(NH_3)_6^{2+}$ and reduction of the 3+ species at the naked electrodes are the same, as suggested by the data in Figure 2.

at the naked electrode. The $Ru(NH_3)_6^{2+}$ is rapidly depleted at the naked electrode and the potential moves away from the solution potential very quickly. When the $Ru(NH_3)_6^{3+/2+}$ concentration is higher, say 10 m$\underline{M}$ in the reduced and oxidized forms, the naked electrode is held closer to the solution potential and does not "overshoot" to a positive potential in the early times after a step from off to on. The "overshoot" problem disappears entirely when the current at the $[(BPQ^{2+/+})_n]$-coated electrode is limited by the polymer. In this case the current at the naked electrode is less than the mass transport limited current leaving a significant amount of both halves of the solution redox couple at the naked electrode surface keeping its potential close to that of the solution. When there is not the problem from low $Ru(NH_3)_6^{3+/2+}$ concentration the diode represented by Scheme I has been demonstrated to switch from off to on and achieve the steady-state current within 50 ms. Figure 5 gives data for a microelectrochemical diode that shows such rapid response. The limiting current under forward bias is limited by the polymer at the coverage of $[(BPQ^{2+/+})_n]$ and concentration of $Ru(NH_3)_6^{3+/2+}$ used. Such a microelectrochemical diode could be operated at about 10 Hz.

Conclusion

A two-terminal microelectrochemical diode can be fabricated by coating one microelectrode with a redox active polymer that blocks the oxidation, but allows the reduction, of a solution redox couple that reversibly contacts an adjacent microelectrode. Good steady-state current-potential curves for the diode can be

obtained, but the frequency of operation is limited to the
switching speed of the polymer, about 50 ms for the thickness of
polymer used. The frequency of operation is higher than for a
diode recently fabricated[5] where both redox reagents were
immobilized. However, when one redox reagent is in solution
there is the disadvantage that the device only functions as a
diode when the solution redox couple is present. The
microelectrochemical diode described in this article illustrates
that control of device characteristics is possible by
manipulating molecular properties such as those that would change
redox potentials therby changing the threshold voltage. The
practical value of the diode described is that it allows
assessment of synthetic methodologies, characterization of
materials properties, and illustrates principles that could be
exploited to develop new kinds of devices. Actual use of the
microelectrochemical diode as an electronic device is unlikely,
but the ability to rationally functionalize microelectrodes is an
important step in being able to develop new kinds of chemical
sensors using microelectrode arrays.[6]

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FIGURE CAPTIONS

Figure 1. Cyclic voltammetry, 100 mV/s, characterization of one derivatized microelectrode of an eight-electrode array. The coverage of electroactive $[(BPQ^{2+/+})_n]$ polymer is 3.4×10^{-8} mol/cm^2. No electroactive material was detected at any of the other seven, naked, microelectrodes of the same array. Scheme II represents the array characterized in this and Figures 2-4.

Figure 2. Cyclic voltammetry response, 50 mV/s, of derivatized and naked microelectrodes in a 0.1 $\underline{M}$ KCl solution containing 2 m$\underline{M}$ $Ru(NH_3)_6^{3+}$ (left) or 1 m$\underline{M}$ of $Ru(NH_3)_6^{3+}$ and 1 m$\underline{M}$ of $Ru(NH_3)_6^{2+}$ (right). The solution containing the $Ru(NH_3)_6^{2+}$ was generated by electrochemical reduction of the 2m$\underline{M}$ 3+ species. The 1mM/1mM concentrations are only approximate, ~20%. Note that the derivatized electrode, the top curve for both solutions, is incapable of oxidizing $Ru(NH_3)_6^{2+}$ and only capable of reducing $Ru(NH_3)_6^{3+}$ when the $[(BPQ^{2+})_n]$ begins to become reduced at about -0.4 V vs. SCE. The naked microelectrodes respond reversibly to the $Ru(NH_3)_6^{3+/2+}$ redox system.

Figure 3. Steady-state current-voltage curves for a two-terminal diode device (smooth curve) as represented in the inset sketch compared to the response for a two-terminal device involving two naked electrodes (dashed curve).

Figure 4. Current-time behavior of the two-terminal diode characterized by the steady-state data in Figure 3 upon switching
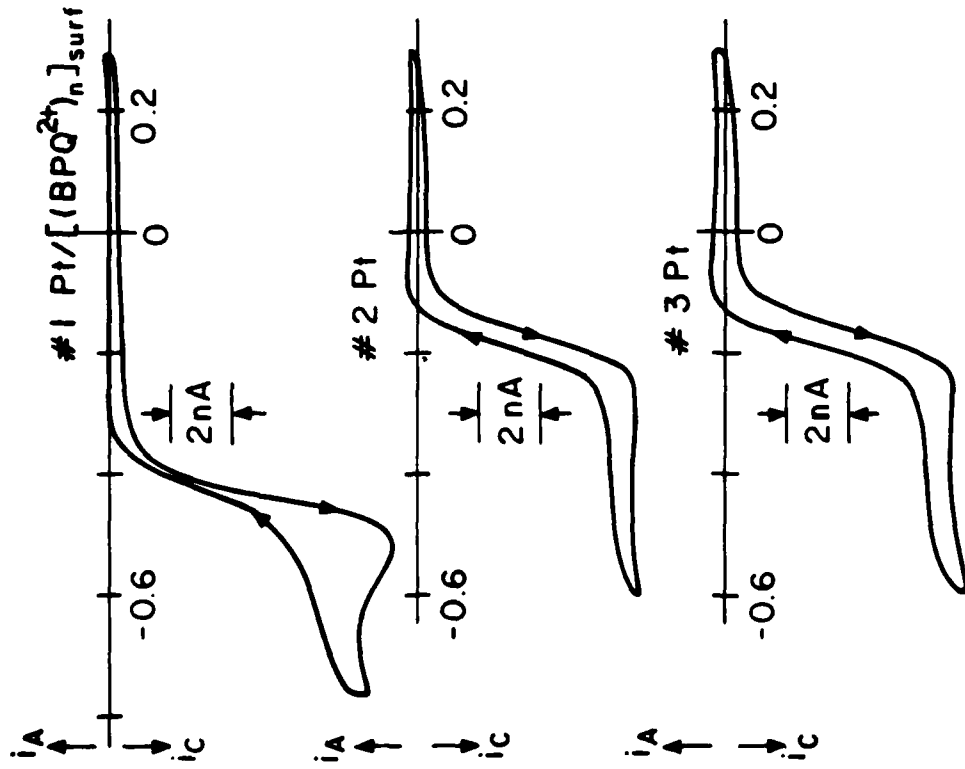
from the off (-0.6 volts applied) to the on (+0.6 volts applied) states.

Figure 5. Characterization of two-terminal devices in 1.0 $\underline{M}$ KCl containing 3.8 m$\underline{M}$ of both $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$. The dashed curve shows the steady-state current-voltage relationship for two adjacent naked electrodes, and the smooth curve shows the steady-state current-voltage relationship for one naked electrode and and an adjacent electrode derivatized with 0.9×10^{-8} mol/cm^2 of the $[(BPQ^{2+})_n]$ polymer. The inset shows the current-time dependence of the diode upon bias changes between +0.7 and -0.7 V.
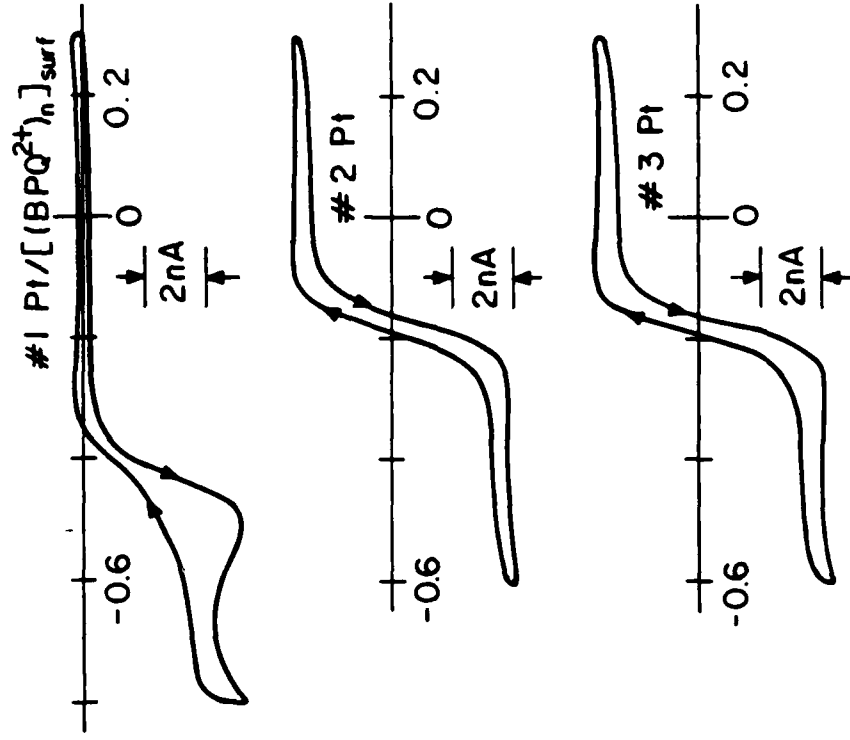
0.1 M aq. KCl, 100 mV/s

Pt / [(BPQ^{2+})$_n$]$_{surf}$
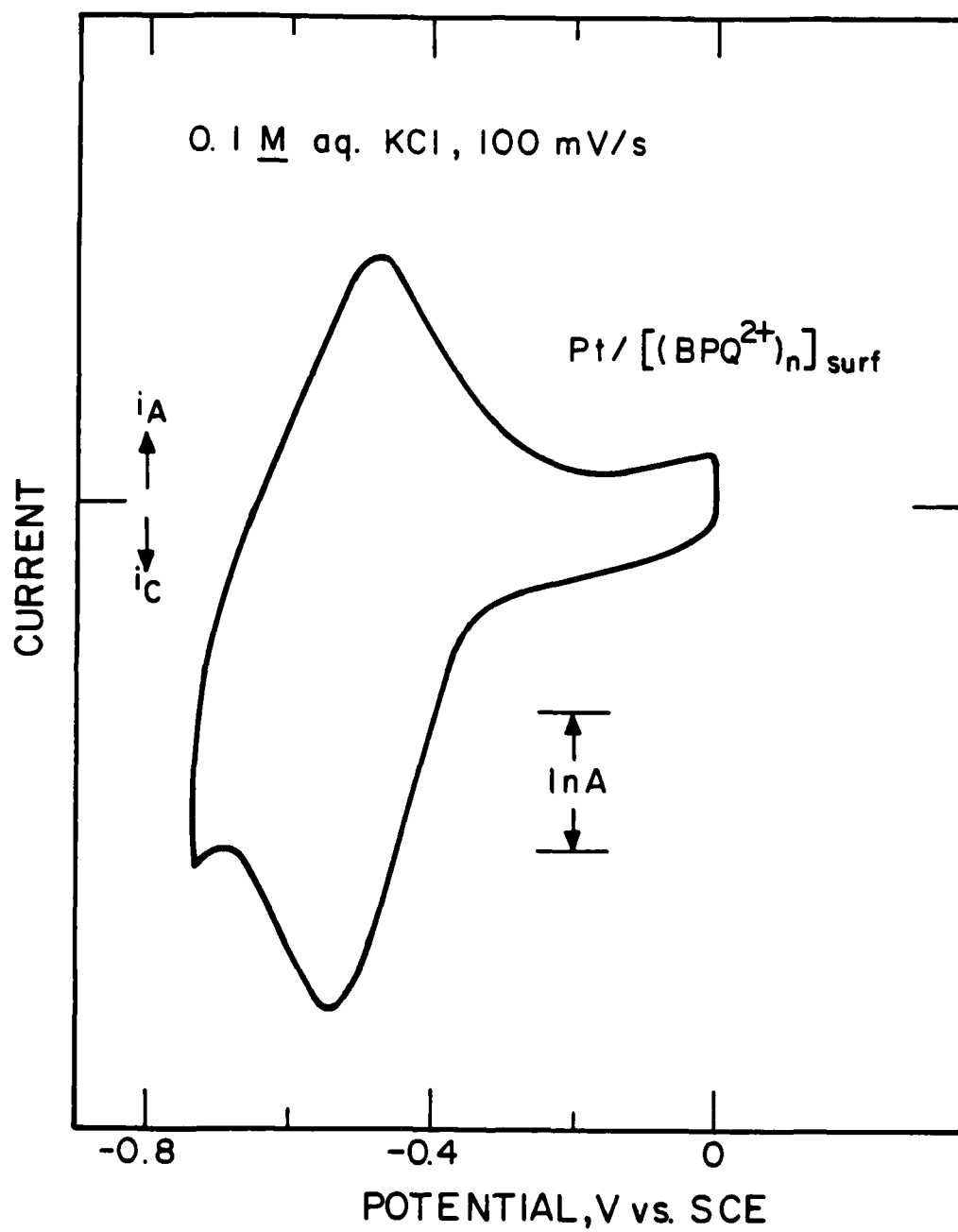
POTENTIAL, V vs. SCE

2 mM Ru(NH$_3$)$_6$Cl$_3$
0.1 M aq. KCl, 50 mV/s

#1 Pt/[(BPQ^{2+})$_n$]$_{surf}$

#2 Pt

#3 Pt

1 mM Ru(NH$_3$)$_6$Cl$_3$, 1 mM Ru(NH$_3$)$_6$Cl$_2$
0.1 M aq. KCl, 50 mV/s

#1 Pt/[(BPQ^{2+})$_n$]$_{surf}$

#2 Pt

#3 Pt

CURRENT

POTENTIAL, V vs. SCE

Two Terminal i-V
Characteristic of
$BPQ^{2+/+}/Ru(NH_3)_6^{3+/2+}$ Diode

$1\,m\underline{M}\;Ru(NH_3)_6Cl_3$
$1\,m\underline{M}\;Ru(NH_3)_6Cl_2$
$0.1\,\underline{M}\;KCl$
$20\;mV/s$

$BPQ^{2+/+/0}$ $Ru(NH_3)_6^{3+/2+}$ Pt

Pt $Ru(NH_3)_6^{3+/2+}$

BIAS (V)
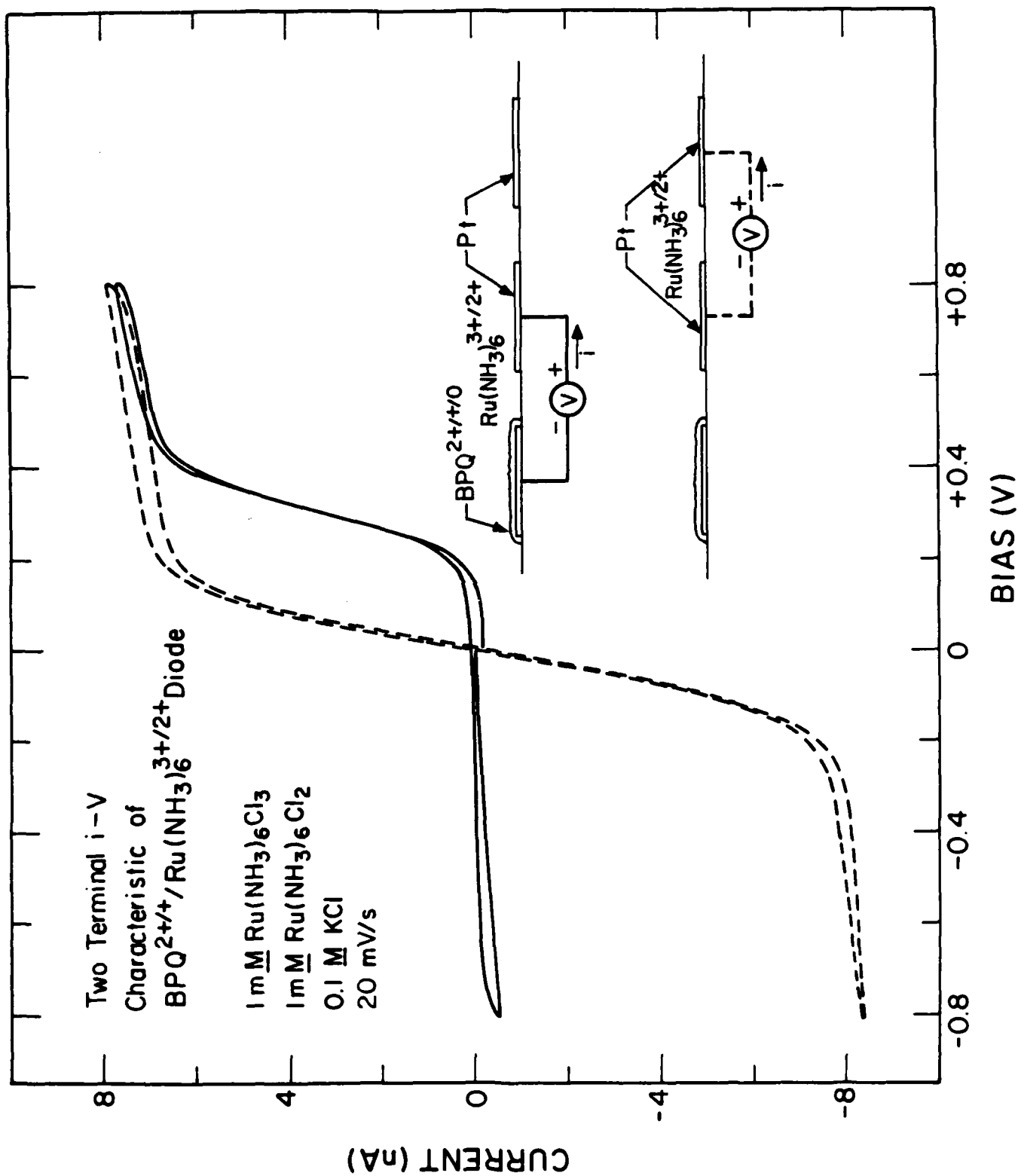
CURRENT (nA)

Frequency Response of BPQ$^{2+/+}$/Ru(NH$_3$)$_6$$^{3+/2+}$ Diode
To a 0.1 Hz Square Wave ± 0.6 V

1mM Ru(NH$_3$)$_6$Cl$_3$
1m M Ru(NH$_3$)$_6$Cl$_2$
0.1 M aq. KCl

← 5sec →

TIME ──→

CURRENT (nA)

8

4

0

-4

Two Terminal i-V
Characteristic of
$BPQ^{2+/+}/Ru(NH_3)_6^{3+/2+}$ Diode

3.8 m$\underline{M}$ $Ru(NH_3)_6Cl_3$
3.8 m$\underline{M}$ $Ru(NH_3)_6Cl_2$
1.0 $\underline{M}$ KCl, 20 mV/s

CURRENT (nA)

BIAS (V)

0.1 Hz Square Wave ±0.7V

5 sec

TIME

CURRENT (nA)

END

FILMED

10-85

DTIC